

**A simple and sensitive gas chromatography- electron capture detection method for
analyzing perfluorocarbon tracers in soil gas samples for storage of carbon dioxide**

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Abstract

Co-injection of a conservative tracer during the geological sequestration of CO₂ can imprint a marker to the injected gas that can be easily recognised during soil gas surveys in case of CO₂ leakage from the reservoir towards the surface.

In this work, an ultra-trace detection method, based on gas chromatography with electron capture detection for analyzing perfluorocarbon tracers (PFTs) in soil gas samples was optimized.

Three totally fluorinated cycloalkane compounds consisting of five and six atom carbon rings were selected for this purpose. We evaluated the feasibility of collecting PFTs on adsorbent tube packed with a commercial graphitized carbon black (CarbotrapTM 100) sampling 2 L of soil gas. The sorbent tubes were then analysed by using a two-stage thermal desorption process.

The developed method allows to quickly determine these compounds at very low fL/L level, method identification limits ranged from 1.3 to 5.8 fL/L. Moreover, it shows good precision, evaluated by within-day and between-day studies.

A preliminary survey of the PFT soil gas background concentrations, conducted by analyzing some soil gas samples collected in two different areas in Central Italy and in the Po Plain, ascertained the PFT background concentration lower than MIL.

Keywords

Perfluorocarbon tracers; soil gas; carbon dioxide storage; leakage monitoring; GC-ECD

1. Introduction

Perfluorocarbon molecules are very stable compounds, they have no biological effects and their atmospheric background concentration is very low, due to their limited commercial use (Lagomarsino, 1996). Moreover, these molecules have a high electron affinities owing to their structure and the large numbers of fluorine atoms, so they are detectable at femtogram levels using an electron capture detector (ECD) or negative ionization chemical ionization mass spectrometry (Cooke et al., 2001). These chemical and toxicological properties made this kind of substances particularly suitable as tracer materials. In particular, the perfluorocycloalkanes have been extensively used to study atmospheric transport and dispersion field programs (Watson et al., 2007), marine surface studies, in house ventilation examinations, and in petroleum reservoir studies (Galdiga and Greibrokk, 2000).

Perfluorocarbon tracers (PFTs) have also been successfully used in some carbon dioxide geological storage projects to monitor and model migration of the injected CO₂ into the reservoir (Vandeweyer et al., 2011, Kharaka et al., 2009, Pamukcu Y. et al., 2011; Morris J. P. et al., 2011). In the same context, another possible application of PFTs is monitoring at surface of eventually CO₂ leaks for the verification of the CO₂ containment in the geological reservoir. In fact the relatively high background levels of soil CO₂ (0-15%) coupled with its seasonal and diurnal modulation, make immediate surface detection of a small CO₂ leak difficult. Co-injection of a conservative tracer during sequestration is a good tool to monitor low level leakage of CO₂ to the surface. This application have been studied only from the National Energy Technology Laboratory of US Department of Energy (Wells et al., 2007) testing PFTs for assessing CO₂ leakages from the Permian Queen Formation where a sequestration pilot study was performed. Successively this approach was applied from the same research group (Strazisar et al., 2009) at a test site in Bozeman (Montana). In both cases the monitoring was carried out at surface measuring tracers concentration in soil gas by passive capillary adsorbent tubes (CATs) that need to be exposed for a long time to soil gas to produce an appreciable signal. This fact, jointly to the difficulty to find these not commercially available samplers makes inconvenient to use CATs as routine systems during the geochemical soil gas surveys.

The aim of this study was to develop a simple and sensitive analytical method for collecting and analysing PFTs in soil-gas samples, and which could be easily carried out during the geochemical surveys adopted in the monitoring of CO₂ storage projects.

2. Material and methods

2.1 Reagents and chemicals

Some properties (and their background atmospheric concentrations) of selected PFTs are given in Table 1. Two of three selected PFTs: perfluoromethylcyclohexane (PMCH, purum quality $\geq 95\%$) and perfluoro-1,2-dimethylcyclohexane (PDCH, purum quality $\geq 80\%$) were purchased from Sigma-Aldrich (St. Luis, MO, USA) whilst perfluoromethylcyclopentane (PMCP, purum quality $\geq 90\%$) was purchased from Fluorochem (UK).

2.2 Instrumentation

The instrumentation used throughout this study was a thermal desorption (TD) autosampler, Master TD, DANI (Italy) coupled to a gas chromatograph fitted with an electron capture detector (GC-ECD) Master GC, DANI (Italy).

2.3 Soil gas sampling

Soil gas surveying consists in collecting and analysing of gas samples from vadose zones. Samples are collected using a hollow steel probe driven into the ground to a depth of 0.6-0.8 m; this depth is considered below the major influence of meteorological variables (Hinkle, 1994; Segovia et al., 1987). The probe was connected, through a silicon hose, to a stainless steel tubes (6.35 mm O.D. x 89 mm) packed with CarbotrapTM 100 graphitized carbon black purchased from Supelco. Air samples were collected at flow rates of 100 ml/min using a portable, constant flow sampling pump (210-1002MTX, SKC, Analitica Strumenti, Italy). Each air sample volume was 2 L. Before use, the packed tubes were desorbed in the TD unit at 350 °C whilst being purged with a stream of helium at 10 ml/min for 30 min and then sealed using Swagelok Teflon end caps. Following sample collection, the tubes were stored in a sealed bag and were analyzed as soon as practicable.

2.4 Sample analysis

The sorbent tubes were analysed by using a two-stage TD process. The tubes were heated (at 330 °C for 10 min) and the volatile compounds were desorbed by a flow of helium at 10 ml/min and transferred to a narrow-bore packed trap filled with Carbotrap[®] and Carbosieve SIII (DANI, Italy), cooled to -20 °C. Once the refocusing step was completed, the trap was heated instantaneously to 330 °C releasing the compounds. These were then introduced, by means of a transfer line (180 °C), directly into the GC injection port (splitless injection at 200 °C) and chromatographed on an Al₂O₃/Na₂SO₄

PLOT column (50 m x 0.32 mm x 8 μ m) supplied from Agilent Technologies (Torino, Italy). The helium flow rate was 3 ml/min. The PFTs were separated using a temperature program: 50 °C for 6 min, then 7 °C/min to 190 °C, then 190 °C for 15 min. Compounds were identified according to their retention times by analysis of individual standard PFT compounds. All PFT compounds were detected using the ECD at 300 °C with a nitrogen flow of 40 ml/min.

2.5 Quantification

PFTs were quantified using external calibration procedure. Calibration of the GC-ECD was accomplished using standards introduced into the analytical system in sample tubes. The tubes were loaded by injecting measured quantities of a standard mixture, determined using volumetric syringes, into a stream of ultrahigh purity N₂ flowing through the tube, as reported in Watson et al. (2007). Standards were run with each set of samples which allowed that variations in instrument performance were quickly identified and corrected. Calibration graphs of signal versus concentration were plotted; the regression equations obtained were used to quantify the unknown PFT concentrations in the soil samples.

2.6 Cautions

Owing to the very low concentration levels revealed the self contamination occurrence is actual. For this purpose, all equipment utilized were carefully checked to be PFT free, frequently performing blank procedure analyses.

3. Results and Discussion

3.1 Sampling and analytical method optimization

In the literature, the only studied sampler system for PFT analysis in soil gas has been the passive type of sampling called CATs. The amount of soil gas the CATs are exposed to during passive sampling is limited by the diffusion rate of air into the open end of the tube. On average, 0.2 L per day is a reasonable approximation for passive sampling rates (Wells et al., 2007), so depending on the concentration of tracer in soil gas CATs have to be exposed from some hours to some days to soil gas to produce an appreciable signal. Keeping detection limits as in Wells et al. (2007), our aim was to drastically reduce the tracer sampling time in order to perform PFT sampling during the normal geochemical soil gas monitoring surveys. The best compromise between sensitivity and accuracy of the

analysis was found sampling 2 L of soil gas, obtaining quantification limits comparable to those reported in literature (Wells et al., 2007) with a very fast sampling time (20 min), being 100 ml/min the maximum flow rate permitted from the sorbent tubes.

The breakthrough occurrence was then evaluated connecting together two adsorbent tubes. For this purpose the first tube was loaded with 400 pg of PFT standard mixture and 2 L of ultrahigh purity N₂ were made to flow through the tubes. No PFTs were observed on the second adsorbent tube. This procedure has been repeated with the flow of 2 L of soil gas sample, and also in this case no PFTs were revealed on the second check tube.

During the desorption step, PFTs desorbed from the tubes were trapped in the cold trap and injected into the analytical column only at the end of desorption cycle. PFT breakthrough from the cold trap during desorption was investigated. 400 pg of PFT standard mixture was loaded onto adsorbent tubes and then desorbed under a range of helium desorption volumes, flow rates and cold trap temperatures to determine the best conditions for minimizing loss of PFTs from the cold trap. Then, desorption temperature and time were optimized in order to obtain the maximum desorption efficiencies for PFTs from the Carbotrap tubes.

3.2 Method performance

A chromatogram of the separation of a standard mixture of the three PFTs loaded onto adsorbent tubes at the level of 100 pg is reported in Figure 1. Four of the six possible PDCHs are resolved, and the elution order is in tune with that found from Galdiga and Greibrokk (2000) using the Al₂O₃ column. The last two peaks of the PDCH isomer family are the two stereoisomers of 1,2-PDCH and the isomer chosen for tracer quantification, was the last one.

As shown in Figure 2, the instrumental response was linearly related to injected amounts of the analytes up to 500 pg, with R² ranging between 0.989 and 0.993.

The within-day and between-day precisions of the analytical method were evaluated analyzing three times soil gas samples spiked with PFTs at three concentration levels: 10, 50 and 100 fL/L. A typical GC-ECD chromatogram resulting from analysis of soil gas sample, spiked with analytes at 10 fL/L concentration, is shown in Figure 3. Results are presented in Table 2. At the spike levels considered, within-day precision was between 5 and 11 %, whilst between-day precision ranged from 6 to 15 %. No comparison can be made about precision because there is no mention of it in the unique available study regarding the analysis of the PFT in soil gas (Wells et al., 2007 nor in reference therein).

Analyte instrumental limits of detection (LODs) were estimated by the GC-ECD chromatogram resulting from the analysis of 10 pg injected from composite standard solution. The peak height-to-averaged background noise ratio (S/N) was measured, and the background noise estimate was based on the peak-to-peak baseline near the analyte peak. Accordingly, a definition of LOD as the amount giving S/N=3 was adopted. Method identification limits (MILs) were estimated in the same way by analyzing a real soil gas sample fortified at 10 fL/L level (data listed in Table 3). As previously stated these limits are comparable to those obtained by analyzing PFT in soil gas (Wells et al. 2007) or in the atmosphere (Watson et al. 2007), in which the analytical detection limits were on the order of 10^{-15} L tracer/L of gas, and slightly better (one order of magnitude) than those reported by Galdiga and Greibrokk (2000) analyzing PFT in reservoir gases.

3.3 Application to real samples

A preliminary survey of the PFT soil gas background concentrations was conducted by analyzing some soil gas samples collected in two different suburban areas, twenty close to Rome city and thirty in Po Plain. Only two samples, the first collected in the first field survey, showed a concentration of PFT higher than MDL. PMCH and PDCH were found in the first sample at concentration of 9.7 and 1.9 fL/L respectively, and only PMCH at 7.8 fL/L was revealed in the second sample. These signals could be probably due to a non perfect sampling system cleaning, at the beginning kept in the same room where PFT standard solutions were prepared. After the sampling system was moved to another laboratory, no tracer signal was detected anymore in the soil gas samples collected in the following field survey. These PFT soil gas background concentrations are in tune with those reported by Cooke et al. (2001, and reference therein), ranging from 0,96 (1,2-PDCH) to 4,6 fL/L (PMCP and PMCH).

Due to local geological structure, soil gas samples taken in Northern Italy were characterized by a higher degree of humidity that implied a more noised chromatographic baseline. We tested the insertion of a filter and/or a desiccant (drierite) trap before the sampling tube. Unfortunately neither of them showed a clear improvement of the baseline, anyway raising the isocratic step at the end of the analysis from 5 up to 15 minutes has partially reduced this drawback.

4. Conclusions

A simple and sensitive TD-GC-ECD method to identify and quantify 3 PFT in soil gas samples was developed. This method, besides being easily reproducible as developed with commercial samplers allows a precise detection of very low quantities of PFT with very short sampling time.

PFT soil gas baseline quantification in Central Italy and in the Po Plain have been carried out successfully, determining a PFT background concentration lower than MIL.

The analytical optimized methodology and the PFT background concentration found in field surveys enable to consider the addition of PFT as an useful tool for monitoring leakage from CO₂ geological storage reservoir with the insertion this type of tracers' monitoring in geochemical monitoring plan for the CO₂ geological storage among the technologies that can detect the presence, location and migration paths of CO₂ at surface.

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241 **Figure Captions**

242 **Figure 1.** Chromatogram of a PFT standard mix (100 pg loaded onto adsorbent tube).

243 **Figure 2.** Instrumental response related to injected amounts of the analytes up to 500 pg.

244 **Figure 3.** GC-ECD chromatogram resulting from the analysis of soil gas sample, spiked with analytes
 245 at 10 fL/L concentration.

Table 1
Properties of PFT compounds investigated.

Acronym	Chemical name	Molecular formula	Molecular weight (g/mol)	Boiling point (°C)	Density at 25 °C (kg/L)
PMCP	perfluoromethylcyclopentane	C ₆ F ₁₂	300	48	1.707
PMCH	perfluoromethylcyclohexane	C ₇ F ₁₄	350	76	1.788
1,2-PDCH	perfluoro-1,2-dimethylcyclohexane	C ₈ F ₁₆	400	102	1.828

Table 2

Within-day and between-day precision of the TD-GC-ECD method for determining PFT compounds in soil gas samples at three concentration levels

Compound	Within-day precision ^a			Between-day precision ^a		
	10 fL/L	50 fL/L	100 fL/L	10 fL/L	50 fL/L	100 fL/L
PMCP	11	9	8	15	12	8
PMCH	10	8	5	8	7	9
1,2-PDCH	7	5	6	11	6	13

^a Mean values from three replications.

Table 3

TD-GC-ECD method performances for analyzing PFT compounds in soil gas

Compound	LOD ^a pg inj	MIL ^b fL/L
PMCP	3	5.8
PMCH	1.5	5.5
1,2-PDCH	0.2	1.3

^a Instrumental limit of detection.^b Method identification limit (S/N=3), estimated analyzing a real soil gas sample fortified at 10 fL/L level.

Figure 1

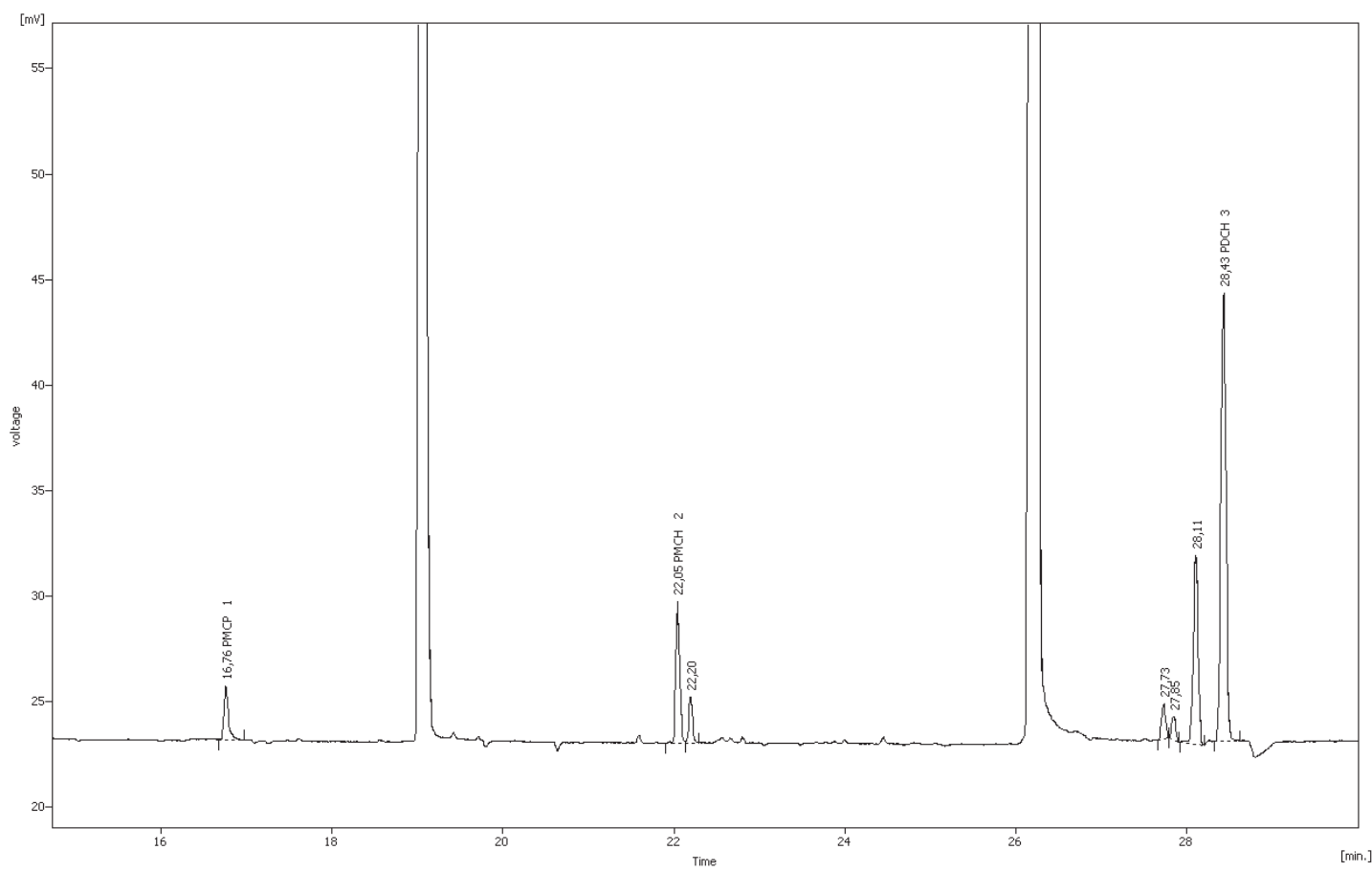


Figure 1

Figure 2

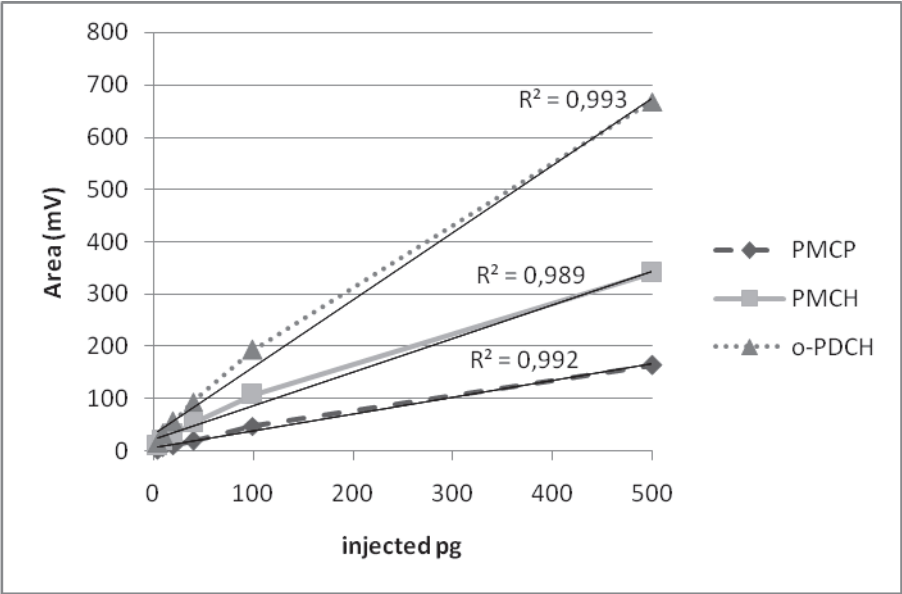


Figure 2

Figure 3

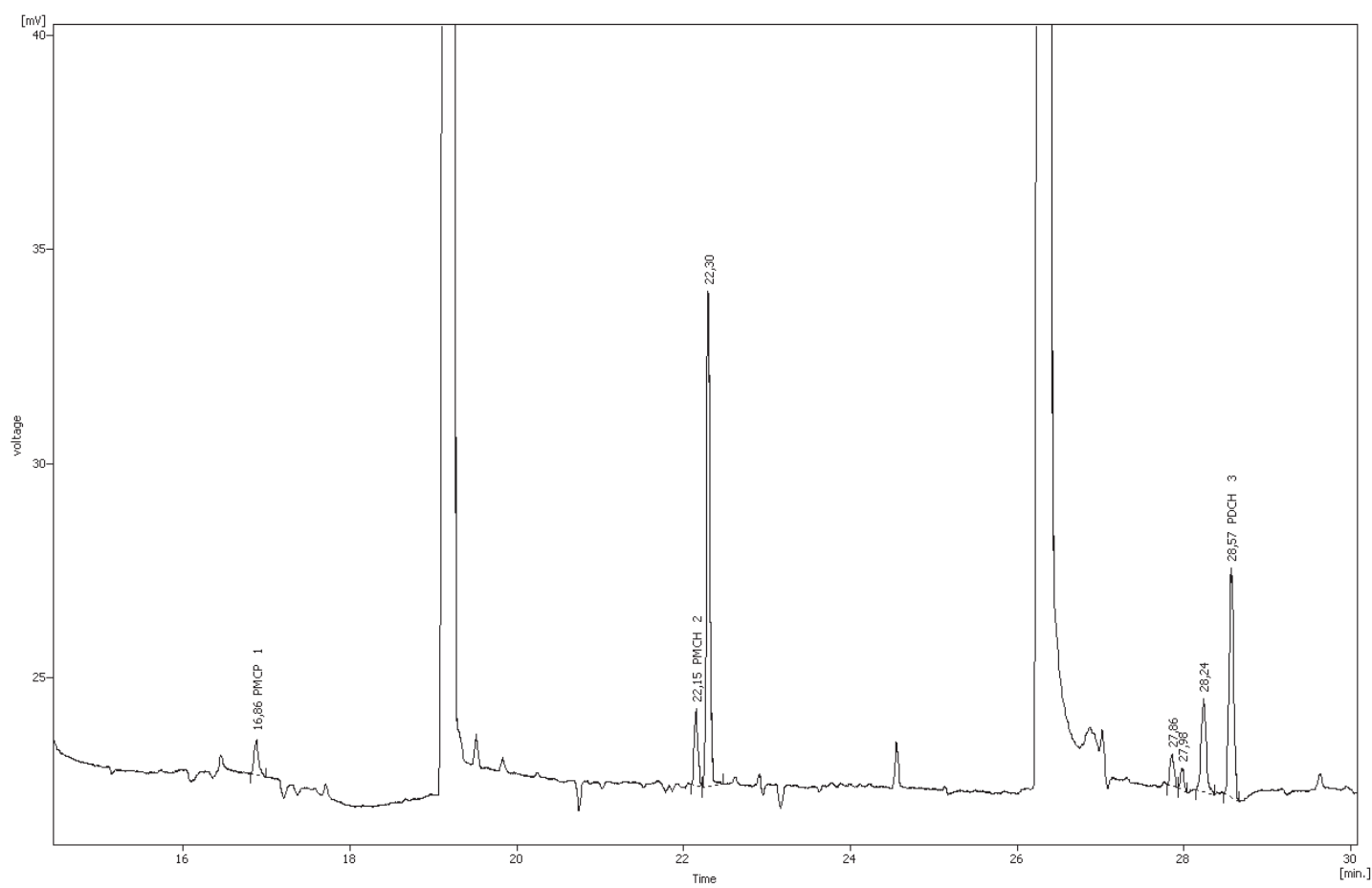


Figure 3